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ELECTRIC FIELD INDUCED RECONSTRUCTIONS IN STM EXPERIMENTS ON Au(111) SURFACES

by

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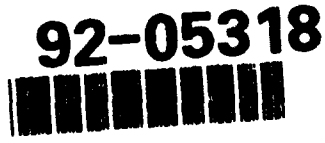

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ABSTRACT

Reconstruction of atomically flat and negatively charged Au(111) surfaces during STM imaging in air is reported. Formation of corrugation line pairs of 0.2 Å height and ~63Å periodic spacing during scanning is attributed to a local electric field induced transition of the surface layer into the $\sqrt{3}$ x 22 reconstructed phase. The concurrent formation of holes and translation of steps during reconstruction suggests that Au(111) allows for both in-plane contraction and in-plane expansion of interatomic bond distances. STM images reveal that the observed corrugated lines in the $\sqrt{3}$ x 22 structure are mobile and anneal into a stable surface structure on the time-scale of tens of seconds.

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Introduction.

Electric field induced rearrangements of surface layer atoms have been a topic of research in field ion microscopy[1] and related theoretical studies for a number of years.[2-4] It has recently been shown, in scanning tunneling microscopy experiments, that the electric field between tip and substrate can modify the spatial structure of adsorbates[5] on semiconductors, as well as the first layer atomic structure of clean semiconductor surfaces[6]. In this report we provide evidence for field-induced reconstruction of the (111) surface of Au during STM imaging. This type of tip-sample interaction is of considerable interest for modifying surfaces at the nanometer level, and may also serve to elucidate aspects of chemical and thermal driven surface reconstructions. Recently observed surface phenomena on Au in STM experiments, including the formations of mounds and pits under the tip[7-9] as well as the movement of steps,[10] may also be related to tip-induced effects.

Au(111) is the only hexagonal close packed surface known to reconstruct, as has been inferred earlier from LEED[11], He-atom scattering[12], RHEED[13] and x-ray[14] data. The exact atomic positions in the unit cell of the $\sqrt{3}$ x 22 reconstruction, however, were revealed only recently by Barth et al.[15] in STM studies performed in UHV. Haiss et al.[16] were the first to show that the $\sqrt{3}$ x 22 surface can be imaged in air and in weakly polar organic solvents. In brief, the reconstructed Au(111) surface is imaged in STM as parallel pairs of corrugation lines (height ~0.2Å) running in the <112> direction with a pair-to-pair separation of ~63 Å. The reconstruction can be rationalized with a tensile stress, arising from charge redistributions of (mainly) sp-electrons in the surface, and inducing an uniaxial compression of the topmost layer interatomic bond distances by 4.3% in the <110> direction. Barth et al.[15] also reported new long range features of this reconstruction on large facets, showing domains separated by ~250 Å and rotated $\pm$ 120° with respect to each other, i.e., zig-zag patterns of parallel lines ("herringbone" pattern). We reproduced most

of the structures known to occur on the reconstructed Au(111) surface in our study, which was performed with the sample being exposed to laboratory air. In addition, however, our results demonstrate that the $\sqrt{3}$ x 22 reconstruction can be induced by STM tip-sample interactions. Electric fields of the order 1V/Å, which are easily achieved in STM experiments, are suspected to displace the first atomic layer of some metals, including Au[2]. Both negative and positive fields can lead to field induced first layer relaxations, which may be sufficient to drive the surface into the reconstructed state. Our observations are of relevance to electrochemical studies, too, since the electric fields involved in STM are of similar magnitude as those observed in the electrochemical double layer. In fact, Gao et al.[17,18] recently reported results of in-situ STM studies, revealing reversible potential induced reconstructions on Au(100)[17] and Au(111)[18] electrodes in aqueous electrolytes, in agreement with earlier combined RHEED and cyclic voltammetry studies of Kolb and Schneider[19].

In this paper we restrict ourselves to the case of negative fields, i.e., excess negative charge residing on the Au surface. The effects of excess positive surface charge and the peculiar effects observed when the sample is immersed in a polar solvent will be the subject of a subsequent paper.

Experimental.

A Nanoscope II(TM) Scanning Tunneling Microscope was used[20]. Experiments were performed in air using mechanically cut and polished Pt(70%) - Rh(30%) tips, which were tested on highly oriented pyrolytic graphite substrates prior to the Au experiments. All STM images were recorded in the constant current mode using a scan rate of 8.6 Hz and consist of 400 x 400 data points. Images were typically low-pass filtered once, unless stated otherwise in the figure captions.

The Au surfaces were prepared according to the procedure given by Hsu and Cowley[21]: a 2 cm piece of 99.999% purity Au wire (0.5 mm diameter, Aesar/Johnson

Mathey) was flame cut; Au spheres (1-2 mm diameter) were formed by heating one end of the wire in a H_2/O_2 flame until molten. Upon cooling in Ar or air, highly reflective, optically flat facets appear on the sphere. Some spheres were further annealed in a cooler flame. Au spheres that were not annealed typically displayed large, atomically flat but unreconstructed areas on the facet, while the annealed spheres typically exhibit large reconstructed areas. The Au spheres were mounted in a home built specimen holder, allowing for orientation of a plane facet for STM studies.

Results and Discussion.

Fig. 1 shows typical images obtained on (111) facets of two different Au spheres in air. Fig. 1a documents the well known $\sqrt{3}$ x 22 reconstruction patterns obtained on the facet of a carefully annealed sphere, showing pairs of corrugation lines with a pair-to-pair separation of ~63 Å (height: ~0.2 Å) as well as domains, rotated $\pm$ 120° with respect to each other. These features are in good agreement with previous work[15]. Fig. 1b presents a large triangular shaped facet that was obtained on a sample which has not been annealed and which does not show any corrugation lines. Atomic resolution can be readily achieved on unreconstructed facets, revealing an interatomic spacing of ~2.9Å, in agreement with the interatomic spacing of bulk Au. Although the lateral accuracy of our instrument is not better than $\pm$ 0.1Å, the measured value for the interatomic spacing together with the absence of corrugation lines leads us to the assumption that this surface represents a metastable, unreconstructed Au(111) surface.

The reconstruction of the Au(111) surface to the $\sqrt{3}$ x 22 phase must involve the formation and/or modification of surface vacancies and larger holes as well as movement of surface steps, since the interatomic spacing decreases with the reconstruction and mass transfer of Au is required. These processes can be seen in the series of images presented in Fig. 2. Fig. 2a shows a stable image of a largely unreconstructed area recorded at -0.1 V (sample vs. tip). Upon increasing the bias voltage between sample and tip from -0.1 to -

1.0 (Fig. 2b and 2c), holes appear on the terrace to the right of the step, corrugation lines begin to form, and the shape of the monoatomic step in the middle of the picture changes slightly. Upon decreasing the bias voltage back to -0.1 , the newly created corrugation lines persist on the surface (Fig. 2d). Further ordering of the corrugation lines and the disappearance of holes occurs over a period of ~ 60s (Fig 2e). This tip-induced surface phenomenon is also documented on the terrace to the left of the step. Here, however, a larger part of the surface is reconstructed during and after the high bias voltage scans, i.e., exhibiting the proper line pair spacing of ~63Å in the final image (Fig. 2e). The results shown in Fig. 2 are representative of numerous experiments in which the reconstruction is observed during scanning.

The $\sqrt{3}$ x 22 reconstruction is readily observed at low or high bias scanning on carefully annealed Au surfaces as shown in Fig. 1a. The surface structure of these thermally-annealed samples, as well as the structure of tip-induced $\sqrt{3}$ x 22 reconstructed surfaces, are stable and unaffected by continued STM imaging.

Since the changes in the surface topography do not occur when the surface is scanned with low to moderate bias voltages ($\leq$ - 0.1 V), and since Holland-Moritz et al.[10] have ruled out the possibility of local heating effects under the tip, we conclude that the electric field between tip and sample at high bias must be responsible for the tip-induced reconstructions shown in Figs. 2. Although the feedback system of the instrument retracts the tip from the surface upon increasing the bias voltage in order to keep the tunnel current constant, the electric field is expected to increase since it is inversely proportional to the tip-sample distance, d, whereas the tunneling current is proportional to e^{-d}. The absolute magnitude of the field, however, is difficult to estimate since the absolute value of the tip-sample separation and the tip geometry are not known.

Generally, metal surface reconstructions are thought to be driven by forces on the topmost layer metal ion cores which arise from electronic charge redistributions in the surface layer[22-25]. Details of this charge redistribution are still a topic of controversy; thus,

it is not yet possible to predict the direction of the surface layer atom relaxation. In an attempt to reconcile apparently contradicting experimental findings, Heine and Marks[21] argued that both expansion and contraction of interatomic bonds in the topmost layer are possible for the uncharged Au(111) surface. Both in-plane contraction and an outward force normal to the surface should occur on an atomically flat surface, whereas expansive forces should emerge in the vicinity of a step. The situation is more complicated when excess charge resides on the surface. Gies and Gerhardts[26] have theoretically shown that the density in the electron tail above the jellium edge is increased when a negative electric field is applied (i.e., negative residing on the surface). This increased electron density should cause further relaxations of the atomic positions in the topmost layer, as has been qualitatively shown by Kiejna[4]. In the STM experiment, these relaxations should be localized to the surface region directly beneath the tip. Following previous arguments[21] that the interatomic bonds in the Au surface represent a bifurcation, i.e., a physical system with two or more energy minima, and that the unreconstructed surface represents one of those minima, the effect of a local field may be to drive the system into the contracted and reconstructed phase.

Inspection of Fig. 2 shows that a large portion of the surface exhibits the well-known twinned corrugation lines with the proper spacing of ~63Å following the "field treatment." The series of images in Fig. 2 also indicates that the $\sqrt{3}$ x 22 reconstruction is accompanied by hole formation. The formation of these holes during the establishment of reconstructive (contracted) surface features supports the proposal of Heine and Marks[21], that Au allows for both, in-plane contraction and in-plane expansion of interatomic bonds. We have also observed that monoatomic steps are slightly displaced during the "field treatment," indicating that diffusion from steps may also play a role in the reconstruction process. Clearly, more detailed and careful measurements are needed to quantitatively evaluate the mass transport during the reconstruction process.

Most of the corrugation lines that appear during imaging are not initially separated by the normal 63 Å spacing, as can be seen in Fig. 2b-c (left). In addition, many of the corrugation lines are not straight (or parallel to other lines), but rather appear to meander across the surface in a random fashion. The surface relaxes during subsequent scanning (at high or low biases, Fig. 2d,e), eventually exhibiting a ~63 Å spacing between parallel corrugation lines. This relaxation process does not appear to result in the formation of any new corrugation lines, but does involve the translation and straightening of the corrugation lines, eventually yielding the normal $\sqrt{3}$ x 22 surface phase. The mechanism by which the corrugated lines move across the surface has not yet been established in our studies and is under further investigation. The establishment of the regular 63 Å spacing between corrugation lines is obviously an intrinsic feature of Au. Our observations that the "field treatment" does not effect large area regions exhibiting the ordered $\sqrt{3}$ x 22 (once formed by thermal annealing or by the tip-induced transition) indicates a significantly higher stability of this phase relative to the unreconstructed phase or to the transition state in which the corrugation lines are not properly aligned.

Approaching the end of our discussion we address the possible role that contaminations might play in our experiments. The formation of reconstruction patterns which are known to form only when the surface exhibits a high degree of cleanliness, leads us to the assumption that we are dealing with clean Au. Also, we rule out the possibility that the unreconstructed surface is stabilized by undetected adsorbates, which would be subsequently removed during the scan process, allowing the surface to reconstruct. This should degrade the resolution of the tip or at least increase the noise in the images, neither of which is observed. More importantly, the removal of an adsorbate should be more effective when the tip is very close to the surface, i.e., when the surface is scanned with low bias voltages. However, we did not observe any surface phase transitions when the surface was scanned under low bias voltage conditions. Also we note that the phenomena reported here were reproduced on different samples and with different

tips. Further support not only for the cleanliness aspect but also generally for our proposed mechanism comes from the "in-situ" electrochemical STM studies by Gao et al.[17,18] who were able to atomically resolve reconstructed areas of a flame treated Au(100)[17] and Au(111)[18] electrodes as a function of the applied cell potential. Since the reconstructions take place in a potential range below the onset of specific adsorption, Gao et al. suggested, in close similarity to our argument, that the accumulation of excess negative charge on the surface might act as the driving force for the reconstruction.

Finally, we note that excess surface charge also seems to be responsible for the (1x1) → (1x2) reconstructions observed upon alkali adsorption on some metallic (110) substrates, e.g., Cu(110) (for an overview on these phenomena: see Bonzel[27]). Charge transfer between the adsorbed alkali atom and the metal increases the local surface electronic charge, a situation not too dissimilar from that encountered in our STM experiment (in which the adsorbed alkali ion is replaced by the STM tip in a gedanken experiment). The conceptual similarity of these processes, in conjunction with the present demonstration of a tip-induced reconstruction, suggests interesting applications of STM in fundamental investigations of reconstruction dynamics.

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Fig. Captions.

Figure 1. Typical STM images obtained on annealed and unannealed Au(111) surfaces

(a) large area showing most of the known features of the $\sqrt{3}$ x 22 reconstruction (annealed surface). Bias: +150mV, current: 3nA.

(b) unreconstructed triangular facets on an unannealed surface; Bias: +10mV, current: 2.1nA.

(c) atomically resolved area of an unreconstructed surface. The interatomic spacing is ~2.9 Å. Bias: +10mV, current: 14.9 nA (unfiltered).

Figure 2. Bias- and time-dependent development of reconstruction features on the Au (111) surface. Image processing software was used to adjust the average heights of the terraces (right and left side of the monoatomic step) in order to enhance the contrast associated with the reconstruction lines.

(a) low bias scan, -100 mV, 8nA; $t = t_0$

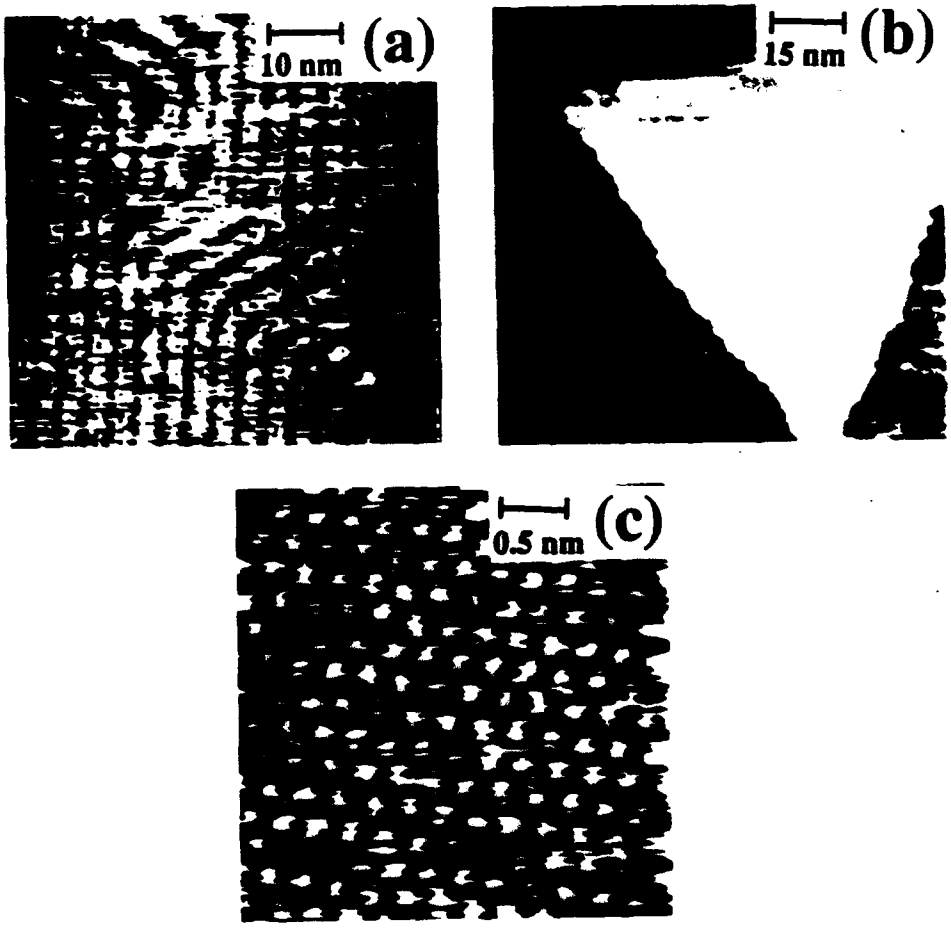
(b) -800 mV, 8nA; $t = t_0 + 60$ sec

(c) -1000 mV, 8nA; $t = t_0 + 120$ sec

(d) -100 mV, 8nA; $t = t_0 + 180$ sec

(e) -100 mV,8nA; $t = t_0 + 240$ sec

Scnott Fig 1 comp



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